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HYDROGEN EMBRITTLEMENT OF DUAL PHASE AND TRIP STEELS

VODÍKOVÁ KŘEHKOST OCELÍ DUAL PHASE A TRIP

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Abstract

The presented paper is devoted to the study of the resistance of two modern steels, dual phase (DP 750) and TRIP 800 steels, used in the automotive industry, to hydrogen embrittlement. Parts manufactured of these steels are zinc galvanized to protect them to corrosion. The acid pickling to activate the steel surface is one of the operations that precede galvanizing. Acid pickling can however provoke hydrogen embrittlement of steels as hydrogen can enter the steels during this operation. The resistance of the DP and TRIP steels to hydrogen embrittlement was studied using tensile tests on previously hydrogen charged specimens. Both steels absorbed different amount of hydrogen depending on the conditions of hydrogen charging. For the same conditions of the hydrogen charging, the amount of hydrogen was much higher in the TRIP 800 steel. It can be attributed to the higher amount of the residual austenite in this steel (8 %). A significant hydrogen embrittlement could be provoked in both steels, which manifested itself mainly by a drop of the plasticity and changes in the failure mode. For the severe conditions of the hydrogen charging, even an irreversible hydrogen embrittlement was observed in the TRIP 800 steel, very probably due to the presence of non-metallic inclusions in the form of stringers, which acted as crack initiation sites. Surprisingly, the TRIP 800 steel did not demonstrate the high resistance to hydrogen embrittlement as generally expected. On the other hand, in conditions simulating industrial acid pickling, no hydrogen embrittlement was observed for the both studied steels.

Abstrakt

Práce je věnována studiu odolnosti moderních ocelí dual phase (DP) a TRIP, používaných v automobilovém průmyslu, vůči vodíkové křehkosti. Z důvodů protikorozi ochrany jsou díly z těchto ocelí zároveň zinkovány. Vlastnímu zinkování předchází moření dílů v kyselinách a zde existuje riziko vyvolání vodíkové křehkosti. Odolnost ocelí DP a TRIP vůči vodíkové křehkosti byla testována pomocí tahových zkoušek na předem vodíkováných vzorcích. V závislosti na podmínkách vodíkování absorbovaly oceli různé množství vodíku. Za stejných podmínek byl obsah vodíku v oceli TRIP podstatně vyšší než v oceli DP, což souvisí s vyšším podílem zbytkového austenitu v této oceli (8 % ve studované oceli). V obou ocelích bylo možné vyvolat výrazné vodíkové zkřehnutí, které mělo v případě oceli TRIP i ireverzibilní charakter. U oceli TRIP se neprokázala vyšší odolnost vůči vodíkové křehkosti pravděpodobně kvůli vyššímu obsahu nekovových vměstků, které byly vyloučeny i ve formě řetízků. Naproti tomu za podmínek simulace moření dílů v kyselinách nebylo pozorováno žádné vodíkové zkřehnutí. Z průmyslového pohledu se tedy zdá, že riziko vodíkové křehkosti těchto ocelí je zanedbatelné.

Key words: Dual phase steel, TRIP steel, hydrogen embrittlement, microstructure, fractography.

1. Introduction

In the automotive industry, materials with high toughness as well as high strength materials are required for the construction of car bodies or especially crash absorbent elements. Advanced high strength steels (AHSS) have been developed to meet the demands of weight reduction, improved passive safety features, energy saving considerations and environmental protection [1-3]. These AHSS steels, which are mostly multiphase steels, show an excellent combination of high strength and good formability. These types of steels, particularly DP and TRIP steels are very sensitive to all post-processing operations, for example to hot-dip galvanizing to provide corrosion protection [4]. The use of thinner cross-section parts makes corrosion protection very important in order to maintain structural integrity and satisfy durability expectations [5]. Several technological operations precede galvanizing, among them also acid pickling. Its purpose is mainly to clean and "refresh" metal surface prior galvanizing. However, acid pickling represents a risk of hydrogen embrittlement as hydrogen can enter the steels during this operation [6,7].

Presented paper is devoted to the study of hydrogen embrittlement of two AHS steels – DP 750 and TRIP 800 steels after electrolytical hydrogen charging and in conditions simulating industrial acid pickling.

2. Experiments, results and discussion

Thin sheets made of two different steels – DP 750 and TRIP 800 steels - were used in this study. The chemical composition of the steels is given in Table 1. Both steels were industrially manufactured. The thickness of the DP 750 steel sheet was 1.2 mm, the thickness of the TRIP 800 sheet was 1.5 mm. The supplier has given no details concerning sheet manufacturing process.

Table 1 Chemical composition of the steels (mass %)

Steel	C	Mn	Si	P	S	Cr	Mo	Cu	Ni	Al
DP750	0.14	1.92	0.21	0.016	0.001	0.02	0.02	0.02	0.02	0.024
TRIP800	0.22	1.65	1.71	0.020	0.004	0.03	0.01	0.02	0.02	0.043

The mechanical properties of the steels in the as-received state are summarised in Table 2. Both steels have rather low yield strength (YS) to ultimate tensile strength (UTS) ratio. TRIP 800 steel shows high value of elongation (29.5%), which is typical for this kind of steels [8].

Table 2 Mechanical properties of the steels

Steel	Yield Strength YS (MPa)	Ultimate Tensile Strength UTS (MPa)	Elongation EL (%)	YS/UTS
DP750	458	737	17.4	0.62
TRIP800	596	948	29.5	0.63

Steel microstructures were studied using light microscopy (LM) and scanning electron microscopy (SEM). They are shown in Fig. 1 and 2. The microstructure of DP 750 steel consists of ferrite and martensite (Fig. 1). The quantitative structure analysis, to determine the amount of ferrite and martensite, has not been performed. TRIP 800 steel has the microstructure consisting of ferrite, bainite and martensite. Fine carbide particles can be observed in the microstructure of the TRIP 800 steel. Two different micrographs are presented for the TRIP steel. The first one is after conventional Nital etching (Fig. 2a), the second one (Fig. 2b) is after special coloured etching by Le Pera [9]. For Le Pera etching, it is assumed that ferrite is blue coloured, bainite is brown and regions containing a high amount of austenite are white.

Residual austenite content was evaluated by X-ray analysis. No residual austenite was found in the DP 750 steel, which implies that austenite content is below the detection limit (<approx. 2 %).

8 % of residual austenite was found in the TRIP steel. This value is somewhat lower than recommended content (10 – 15 % of residual austenite) [8] but mechanical properties are quite satisfactory.

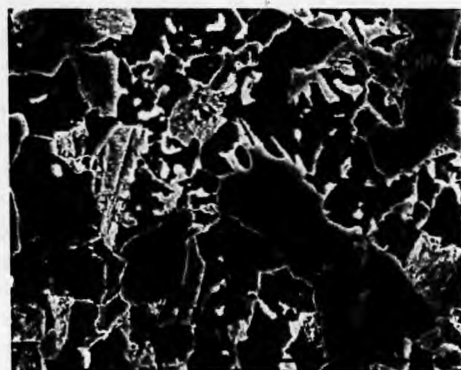


Fig. 1 Microstructure of the DP 750 steel (Nital etching, SEM)

Resistance of the steels to hydrogen embrittlement was tested using tensile tests on previously hydrogen charged specimens. Hydrogen charging was performed electrolytically in 1M solution of nitric acid at different current densities (from 15 to 30 mA·cm⁻²). In some cases, As₂O₃ was added into the solution (5 mg·l⁻¹) as the hydrogen absorption promoter [7]. Hydrogen charging took 4 hours at ambient temperature. Four hours were sufficient taking into account rather low specimen thickness (1.2 or 1.5 mm). Hydrogen content in the steels was evaluated by vacuum extraction at 600°C. By this method, the entire hydrogen content is not evaluated but only that part which is not trapped irreversibly at this temperature [10].



a) Nital etching, SEM

b) Le Pera etching, LM

Fig. 2 Microstructure of the TRIP 800 steel

During tensile tests, higher hydrogen content provoked less or more pronounced embrittlement in both steels, which manifested itself mainly by a drop of elongation. Hydrogen embrittlement index I_{emb} could be calculated in accordance with the following equation:

$$I_{emb} = \frac{EL_0 - EL_H}{EL_0} \cdot 100 \quad (\%), \quad (1)$$

where EL_0 is elongation in the as-received state (without hydrogen charging)

and EL_H is elongation after hydrogen charging.

Table 3 shows the values of hydrogen embrittlement index I_{emb} for both steels and different conditions of hydrogen charging. The values of the hydrogen content in the steels are given as well. It is evident from the presented results that As_2O_3 is a very potent promoter of hydrogen absorption in the steels. In addition, it can be seen that for the same conditions of the hydrogen charging the TRIP steel absorbs much more hydrogen in comparison with the DP steel. This behaviour of the TRIP steel can be attributed to the higher amount of residual austenite in the structure. The residual austenite acts as irreversible trap at ambient temperature and it can absorb a high quantity of hydrogen. It results in decreasing hydrogen content in ferrite (bainite), which by implication increases diffusion hydrogen flux into the steel. Hydrogen flux is proportional to the concentration gradient in accordance with the Fick's first law. Ly [11] has found out that the surface hydrogen concentration is much higher in the TRIP steel during electrochemical permeation tests in comparison with some other kinds of steels (DP and CP steels). Furthermore, it can be deduced from Table 3 that an important hydrogen embrittlement can be provoked in the both studied steels. The presence of a higher amount of residual austenite in the TRIP steel does not seem to be very beneficial. It can be also related to the size and shape of residual austenite regions [8] but this analysis has not been performed in the presented study.

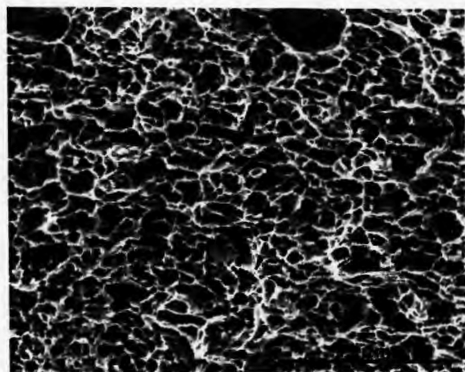
Table 3 Hydrogen embrittlement index and hydrogen content in the studied steels

Steel	I_{emb} (%)	H content (ppm)
DP as-received	0	0.2-0.3
DP750 (15mA·cm ⁻²)	9	1.5
DP750 (30mA·cm ⁻²)	14	2.2
DP750 (15mA·cm ⁻² + As ₂ O ₃)	48	4-7
TRIP800 as-received	0	0.3-0.6
TRIP800 (15mA·cm ⁻²)	28	4.5
TRIP800 (30 mA·cm ⁻²)	61	8.8
TRIP800 (15mA·cm ⁻² + As ₂ O ₃)	88	35-40

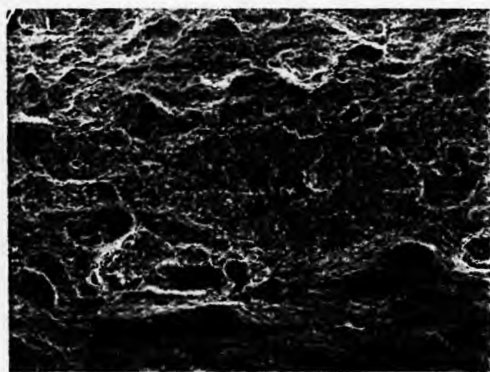
Fractographic analysis revealed that hydrogen charging without As_2O_3 addition resulted only partially in the change of the failure micro mechanism for the DP 750 steel. In this steel, the failure was still predominantly transgranular ductile with dimple morphology, even after hydrogen charging. Nevertheless, the dimples were shallower in the presence of hydrogen. Profile analysis performed for DP 750 steel showed that in the as-received state the average dimple depth was $3.8 \pm 0.3 \mu\text{m}$. After hydrogen charging at the current density of 15mA·cm⁻² for 4 hours, the average dimple depth was only $2.4 \pm 0.2 \mu\text{m}$ (Fig. 3a).

In the TRIP 800 steel, special defects provoked by hydrogen were observed on the fracture surfaces – so called “fish eyes”. Fish eyes represent less or more circular areas of quasi-cleavage fracture around non-metallic inclusions, which act as the crack initiation sites. An example of a fish eye found in the TRIP 800 steel is given in Fig. 3b.

For higher hydrogen content in the steels, if As_2O_3 was used as hydrogen absorption promoter, very important embrittlement was observed for the both steels. For the DP 750 steel, the fracture was nearly entirely transgranular cleavage (Fig. 4a). For the TRIP steel even irreversible cracking was observed. Fig. 4b shows an example of the fracture surface of the TRIP steel. Large cracks perpendicular to the fracture surface area can be observed there. These cracks were very probably initiated already during hydrogen charging prior to tensile testing on stringers of non-metallic inclusions observed in this steel (Fig.5).

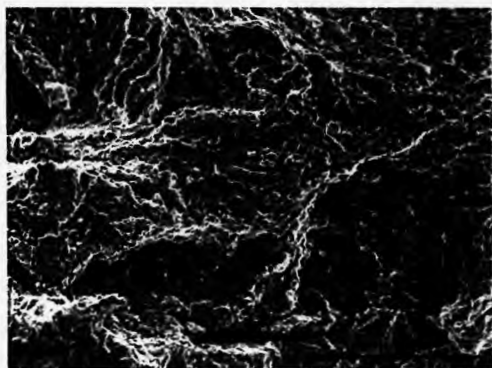


a) dp steel after hydrogen charging at $15\text{mA}\cdot\text{cm}^{-2}$ for 4 hours

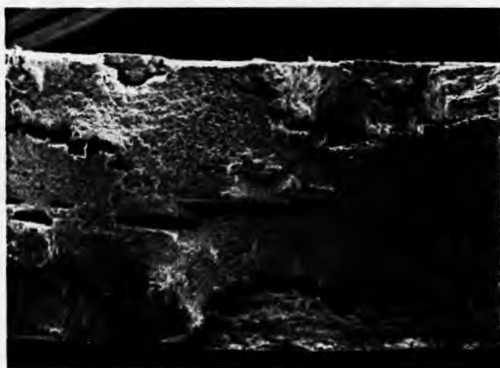


b) trip steel after hydrogen charging at $15\text{mA}\cdot\text{cm}^{-2}$ for 4 hours

Fig. 3 Fracture surfaces of the dp and trip steels after hydrogen charging without As_2O_3 addition



a) dp steel after hydrogen charging with As_2O_3 addition at $15\text{mA}\cdot\text{cm}^{-2}$ for 4 hours



b) TRIP steel after hydrogen charging with As_2O_3 addition at $15\text{mA}\cdot\text{cm}^{-2}$ for 4 hours

Fig. 4 Fracture surfaces of the dp and trip steels after hydrogen charging with As_2O_3 addition

Generally, high resistance to the hydrogen embrittlement is expected in the case of the TRIP steels, mainly thanks to the higher content of residual austenite. It is believed that residual austenite acts as beneficial traps for hydrogen. However, as mentioned above, this beneficial effect depends strongly on the size and shape of residual austenite regions [8]. The presented results show, however, that the resistance of the TRIP steel to the hydrogen embrittlement can be rather poor if all the other requirements are not met. In the presented case, the TRIP steel contained a higher amount of non-metallic inclusions even in the form of stringers, which reduced its resistance to the hydrogen embrittlement.

In addition, an experiment was performed to simulate industrial conditions during acid pickling of the steels prior the zinc coating. Tensile specimens were immersed in the 18.5% solution of the hydrochloric acid for 30 minutes. After that, tensile tests were performed and hydrogen content in the specimens was also evaluated. No hydrogen embrittlement was observed in this case. Both the results of tensile tests and the hydrogen content in the steels corresponded to the values found for the as-received state of the steels. It seems that the risk of hydrogen embrittlement of DP and TRIP steels is very low, even negligible, during the acid pickling.

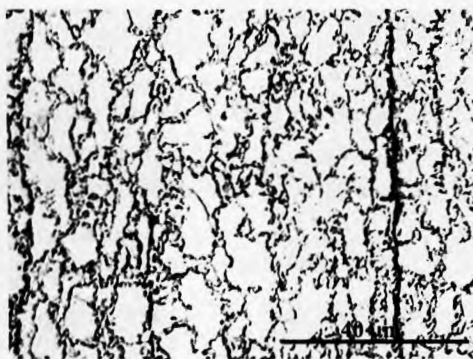


Fig. 5 Stringers of non-metallic inclusions in the TRIP 800 steel

3. Conclusions

Resistance of DP and TRIP steels, used in the automotive industry, to the hydrogen embrittlement was studied. Both steels can be embrittled to different levels depending on the hydrogen charging conditions and hydrogen content in the steels. The TRIP 800 steel absorbs much more hydrogen in comparison with the DP 750 steel due to the higher residual austenite content. However, its resistance to the hydrogen embrittlement is not excellent very probably due to the higher content of non-metallic inclusions presented even in the worst morphology of stringers. Irreversible cracking can be provoked in this steel for the severe conditions of the hydrogen charging. On the other hand, in industrial conditions, during acid pickling of the steels, the risk of hydrogen embrittlement seems to be negligible.

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